

## LETTER TO THE EDITOR

# A new description of spin tunneling in magnetic molecules

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**Abstract.** A new approach is used that allows to describe the magnetic molecules main properties in a direct and simple way. Results obtained for the  $Fe_8$  cluster show good agreement with the experimental data.

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In recent years, with the experimental advances in the measurement of magnetic molecular clusters properties, it has emerged a new frontier in this area. One of the interesting aspects that came out of these studies is the possibility of measuring spin tunneling in mesoscopic systems what corresponds, in a standard quantum description, to the tunneling of the collective degree of freedom corresponding to the magnetization direction through a potential barrier separating two minima of an effective potential associated with the spatial orientation[1, 2, 3, 4, 5, 6, 7, 8].

From the theoretical point of view, spin tunneling has been treated mainly by the use of a WKB method adapted to spin systems[9, 10], by using Feynman's path integral treatment of quantum mechanics[11, 12], and also by using  $su(2)$  coherent states[13] in order to establish a correspondence between the spectrum of the spin system with the energy levels of a particle moving in an effective potential[14].

In the present letter we intend to show that still another approach may be used for describing spin tunneling – in angle representation – in such a way that analytic expressions for the characteristic parameters of the magnetic molecular clusters can be obtained; in particular, the results for the spectrum and energy barrier heights are directly obtained and the spin tunneling process can be easily interpreted.

The starting point of the present approach is the introduction of a quantum phenomenological Hamiltonian describing the spin system, written in terms of angular momentum operators obeying the standard commutation relations, and that reflects

the internal symmetries of the system. It may also contain terms taking into account external applied magnetic fields. The degree of freedom that undergoes tunneling is considered a particular collective manifestation of the system, and it is assumed to be the only relevant one. At the same time, the temperature of the system is assumed so conveniently low that possible related thermally assisted processes are not taken into account so that only quantum effects are considered. For instance, the general quantum Hamiltonian – sometimes also called giant spin model –

$$H = AJ_z - DJ_z^2 + \frac{E}{2} (J_+^2 + J_-^2) \quad (1)$$

can be used to study some systems of interest. In particular, this Hamiltonian can describe the octanuclear iron cluster[15],  $Fe_8$ , in the presence of an external magnetic field along the  $z$  axis if we take  $A = g\mu_B H_{\parallel}$ ; by taking  $A = 0$  no external field is considered. This spin system has a  $j = S = 10$  ground state and a suggested pure quantum spin tunneling below  $0.35\text{ K}$ ; furthermore  $D/k_B = 0.275\text{ K}$ ,  $E/k_B = 0.046\text{ K}$  [6, 8], and  $k_B$  is Boltzmann's constant respectively. On the other hand, from a pure algebraic model point of view, it is interesting to see that the Lipkin quasi-spin model[16] of wide use in many-body physics is also obtained by just considering  $D = 0$ . At the same time that the Hamiltonians in both cases are similar, and in this form we can compare their results, our interest in this model also resides in the fact that it stands for a valuable testing ground for checking the validity of approximations in treating collective degrees of freedom.

In what follows we will show how we can discuss the spin tunneling process in the  $Fe_8$  cluster by the use of a new Hamiltonian that is an approximate version of Eq. (1). This new Hamiltonian is obtained through a series of transformations performed on the matrix generated by calculating the expectation values of Eq. (1) with the  $su(2)$  coherent states  $|j, z\rangle$ , where  $z$  is a complex variable and  $j$  characterizes the angular momentum state multiplet[13]. The Hamiltonian is the overcomplete spin coherent states representation then given by

$$\langle j, z' | H | j, z \rangle = K(z', z), \quad (2)$$

the also known generator coordinate energy kernel[17], embodies the quantum information related to the system we want to study. The procedure of extracting a new Hamiltonian – written now in terms of an angle variable – from Eq. (2) has been already shown elsewhere and will not be repeated here [18, 19, 20]. In fact, as it was proved there, the variational generator coordinate method can in this case be used to rewrite the Hamiltonian from which we start in an exact and discrete representation which can then be conveniently treated in order to give an approximate Hamiltonian in the angle representation. It is important to point that the Hamiltonian we obtain is in fact an approximate one, but we have also shown, by studying the Lipkin model, that it is already a reliable Hamiltonian for spin systems with  $j = S \gtrsim 5$ , as it is the case for the  $Fe_8$  cluster, when  $S = 10$ , as mentioned before. Furthermore, since this approach is based on quantum grounds from the beginning, it does not need to go through any

quantization process. Also, it is not necessary to convert the discrete spin system into a continuous one as it is usually done[21], at the same time that the quantum character of the angle-angular momentum pair is properly taken into account.

The Hamiltonian in the angle representation associated with the  $Fe_8$  cluster in the absence of an external magnetic field is then written explicitly as

$$H(\phi) = -\frac{1}{2} \frac{d}{d\phi} \frac{1}{M(\phi)} \frac{d}{d\phi} + V(\phi), \quad (3)$$

where

$$V(\phi) = -(D - E) S(S + 1) \cos^2 \phi - ES(S + 1) \quad (4)$$

is the potential energy, whereas the effective “mass” is given by

$$M(\phi) = \frac{1}{2(D - E) \cos^2 \phi + 4E}, \quad (5)$$

with  $-\pi < \phi \leq \pi$ . It is important to observe that the effective “mass” is not constant over the angle domain and that it plays an essential role in this description. Figure 1 shows the potential function as well as the effective “mass”. The minima of both functions occur at  $\phi = 0, \pi$  while the maxima occur at  $\phi = \frac{\pi}{2}, \frac{3\pi}{2} (= -\frac{\pi}{2})$ , as expected.

The eigenvalues and eigenfunctions associated with the Hamiltonian (3) can then be directly obtained by numerically solving the Schrödinger equation

$$H(\phi) \psi_k(\phi) = \mathcal{E}_k \psi_k(\phi) \quad (6)$$

by means of a Fourier analysis. The ground state energy thus obtained,  $\mathcal{E}_{gs} \simeq -27.6447 K$ , agrees quite well with the result obtained by numerically diagonalizing the exact phenomenological Hamiltonian Eq. (1) within the  $|j = S, m\rangle$  state basis (hereafter these results will be called the reference values), specifically, the deviation from the reference value is of the order of 0.5%. Figure 2 depicts the wave functions associated with the lowest pair of energy eigenstates. In what concerns the energy splitting of those states, we obtain a result that is of the same order of magnitude as the reference value; in fact, the deviation is of the order of 17.5%, being that our result is smaller than the reference value.

Now, we see that the top of the potential barrier is explicitly given by

$$V_{\max}(\phi) = -ES(S + 1) \quad (7)$$

so that

$$h_b = -ES(S + 1) - \mathcal{E}_{gs} \quad (8)$$

measures the ground state energy barrier. Using our result for the ground state we get  $h_b \simeq 22.58 K$ , which is only 1.7% higher than the experimental result, namely 22.2 K, presented in [6]. An approximate analytic expression for the ground state energy barrier can be obtained from another perspective. To this end, we first take into account that

$$\mathcal{E}_{\min} = V(\phi = 0) = -DS(S + 1) = -30.25 K, \quad (9)$$

and we also assume that the ground state energy is approximately given by  $\mathcal{E}_{gs} \simeq \mathcal{E}_{\min} + \omega/2$ . We then perform a harmonic approximation at the potential minimum,

$$M(\phi) \omega^2|_{\phi(\mathbf{E}_{gs})} = \frac{d^2 V(\phi)}{d\phi^2}|_{\phi_{\min}}, \quad (10)$$

from which we obtain

$$\omega = 2\sqrt{(D-E)[ES(S+1) + |\mathcal{E}_{gs}|]}. \quad (11)$$

Taking advantage of this dependence on  $|\mathcal{E}_{gs}|$  we obtain the analytic expressions

$$|\mathcal{E}_{gs}| = DS(S+1) + \frac{D-E}{2} \left[ 1 - \sqrt{1 + 4\frac{D+E}{D-E}S(S+1)} \right] \simeq 27.52 K, \quad (12)$$

and

$$h_b = (D-E)S(S+1) + \frac{D-E}{2} \left[ 1 - \sqrt{1 + 4\frac{D+E}{D-E}S(S+1)} \right] \simeq 22.46 K \quad (13)$$

for the ground state energy and barrier respectively. The deviation in the ground state energy is then 0.08% while for the barrier height it is 1.17%. Even if we consider the crude approximation  $(D+E)/(D-E) \sim 1.0$  we get

$$|\mathcal{E}_{gs}| \simeq DS^2 + ES = 27.96 K, \quad (14)$$

and

$$h_b \simeq (D-E)S^2 = 22.90 K, \quad (15)$$

respectively; the value for the barrier height still is in good agreement with the experimental result.

Now, if an external magnetic field paralel to the  $z$  axis is applied the potential function reads

$$V(\phi) = -(D-E)S(S+1)\cos^2\phi - \sqrt{S(S+1)}g\mu_B H_{\parallel} \cos\phi - ES(S+1), \quad (16)$$

while the expression for the effective “mass” is given by

$$M(\phi) = \frac{1}{2(D-E)\cos^2\phi + \frac{g\mu_B}{S}H_{\parallel}\cos\phi + 4E}. \quad (17)$$

It is immediate to see that the presence of the magnetic field does not change the position of the potential minima,  $\phi = 0, \pi$ , but it introduces a shift in energy at these points so that the difference in the height between the two minima will be ( $H_{\parallel} > 0$ )

$$V(\phi = \pi) - V(\phi = 0) = 2\sqrt{S(S+1)}g\mu_B H_{\parallel}. \quad (18)$$

This means that for some particular values of  $H_{\parallel}$  there will occur a degeneracy in the energy spectrum such that the state with, for instance,  $m = n$  will match its energy with that of the state with  $m' = -n + k$ , as it is indeed expected. The particular value of the magnetic field increment  $H_0$  that leads to the matching of the energy levels, therefore given rise to the appearance of the degeneracies,  $H_{\parallel} = k H_0$ , can be obtained from an analysis of the effective “mass” expression. Realizing that the presence of zeroes in the

function  $I(\phi) = 1/M(\phi)$  (infinities of the effective “mass”) indicates that tunneling cannot occur, we look for the expression for the strength of  $H_{\parallel}$  beyond which tunneling will not take place. A direct calculation shows that the limit is given by

$$H_{\parallel}^{\text{lim}} = \frac{4Sk_B}{g\mu_B} \sqrt{2E(D-E)} \simeq 4.32 \text{ T} \quad (19)$$

so that

$$H_0 = \frac{H_{\parallel}^{\text{lim}}}{2S} = \frac{2k_B}{g\mu_B} \sqrt{2E(D-E)} \simeq 0.216 \text{ T} \quad (20)$$

for  $g = 2$ . This result is in good agreement with the experimental value  $H_0 = 0.22 \text{ T}$  [6, 8]. It can be immediately seen that for this value of the external parallel magnetic field the original minimum at  $\phi = \pi$  and the maxima at  $\phi = \pi/2$  and  $\phi = 3\pi/2$  have turned into a single maximum of the potential function, while the only surviving minimum is the one at  $\phi = 0 (= 2\pi)$ . This means that, in this particular situation, there is only one direction the spin can be directed at.

In conclusion we have proposed an angle-based description of the spin tunneling in magnetic molecules that can account for the basic results governing this kind of phenomenon. The results obtained in the case of the  $Fe_8$  cluster agree quite well with the experimental data and the interpretations follow in a direct and simple way.

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- [1] R. Sessoli, D. Gatteschi, A. Caneschi, and M.A. Novak, *Nature (London)* **365** (1993) 141.
- [2] M.A. Novak, R. Sessoli, A. Caneschi, and D. Gatteschi, *J. Magn. Magn. Mater.* **146** (1995) 211.
- [3] C. Paulsen, J.-G. Park, B. Barbara, R. Sessoli, and A. Caneschi, *J. Magn. Magn. Mater.* **140-144** (1995) 379, 1891.
- [4] J.R. Friedman, M.P. Sarachik, J. Tejada, and R. Ziolo, *Phys. Rev. Lett.* **76** (1996) 3830.
- [5] L. Thomas, F. Lioni, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, *Lett. Nature*, vol. **383**, Sept. (1996) 145.
- [6] A.-L. Barra, P. Debrunner, D. Gatteschi, Ch.E. Schulz, and R. Sessoli, *Europhys. Lett.* **35** (1996) 133.
- [7] C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli, and D. Gatteschi, *Phys. Rev. Lett.* **78** (1997) 4645.
- [8] A. Caneschi, D. Gatteschi, C. Sangregorio, R. Sessoli, L. Sorace, A. Cornia, M.A. Novak, C. Paulsen, and W. Wernsdorfer, *J. Magn. Magn. Mater.* **200** (1999) 182.
- [9] J.L. van Hemmen and A. Sütto, *Europhys. Lett* **1** (1986) 481; J.L. van Hemmen and A. Sütto, *Physica* **141B** (1986) 37.
- [10] G. Scharf, W.F. Wreszinski, and J.L. van Hemmen, *J. Phys.* **A20** (1987) 4309.
- [11] M. Enz and R. Schilling, *J. Phys.* **C19** (1986) 1765; M. Enz and R. Schilling, *J. Phys.* **C19** (1986) L711.
- [12] E.M. Chudnovsky and L. Gunther, *Phys. Rev. Lett.* **60** (1988) 661.
- [13] A. Peremolov, *Generalized Coherent States and Their Applications*, Springer Verlag, Berlin, 1986
- [14] V.V. Ulyanov and O.B. Zaslavskii, *Phys. Rep.* **216C** (1992) 179.
- [15] K. Wieghardt, K. Pohl, I. Jibril, and G. Huttner, *Angew. Chem. Int. Ed. Engl.* **23** (1984) 77.
- [16] H. Lipkin, N. Meshkov, and A.J. Glick, *Nucl. Phys.* **62** (1965) 188.
- [17] J. Griffin and J.A. Wheeler, *Phys. Rev.* **108** (1957) 311.
- [18] D. Galetti and M. Ruzzi, *J. Phys. A: Math. Gen.* **33** (2000) 2799.

- [19] D. Galetti, B.M. Pimenttel, and C.L. Lima, *Physica* **A351** (2005) 315.
- [20] D. Galetti, Submitted for publication.
- [21] J. Villain, *J. de Phys.* **35** (1974) 27.

## Figure Captions

Figure 1: The potential and effective “mass” functions associated with the  $Fe_8$  cluster with parameters  $D/k_B = 0.275 K$  and  $E/k_B = 0.046 K$ . The interval is taken as  $-\pi/2 < \phi \leq 3\pi/2$  for clarity.

Figure 2:  $Fe_8$  cluster ground state wave function  $\psi_0(\phi)$  and first excited state wave function  $\psi_1(\phi)$ .

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